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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Continuous Process for the Preparation of N-Alkylethylenediamines

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Canada

2093941

A CONTINUOUS PROCESS FOR THE PREPARATION OF N-ALKYLETHYLENEDIAMINES

(D# 81,098-F)

ABSTRACT OF THE DISCLOSURE

A continuous process for the preparation of N-alkylethylenediamines by the reaction of ethylenediamine and an aliphatic aldehyde having at least 8 carbon atoms in the presence of hydrogen and a hydrogenation catalyst is disclosed.

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(D# 81,098-F)

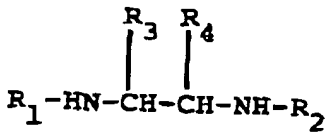
BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for the preparation of N-alkylethylenediamines. More particularly, this invention relates to a continuous process for the preparation of N-alkylethylenediamines by the reaction of ethylenediamine and a long chain aliphatic aldehyde having at least 8 carbon atoms in the presence of hydrogen and, for example, a nickel-copper-chromium catalyst.

2. Prior Art

U.S. Patent No. 3,192,113 to Thomas et al., teaches the preparation of substituted ethylenediamines of the general formula:



wherein R_1 and R_2 are each lower alkyl groups of from 3 to 8 carbon atoms and R_3 and R_4 are hydrogen or methyl prepared by the interaction of amines with ethylene dihalides or by the reductive alkylation of ethylene-diamines with ketones in an inert solvent such as carbon tetrachloride in the presence of hydrogenation catalyst such as platinum or carbon and contacting the suspension with hydrogen in a pressure vessel at a temperature of from about 25° to about 150° C for a period of time up to twenty-four hours.

U.S. Patent No. 3,364,239 to Speranza teaches a method for preparing secondary amino polyoxy alkanols wherein an aldehyde or ketone is reacted with a primary alkoxy monoalkanol to form a Schiff base which is catalytically hydrogenated the secondary amine reaction product. Preferred catalysts include a catalyst having a major amount of (a) nickel or cobalt, (b) copper and (c) a minor amount of at least one normally non-reducible metal oxide such as chromium oxide, molybdenum oxide, etc.

U.S. Patent No. 4,806,690 to Bowman discloses a method for producing amines by contacting at reactive conditions at least one alcohol, aldehyde or ketone or a mixture thereof with an aminating agent such as ammonia

or primary or secondary amines in the presence of a catalyst comprising cobalt, copper and a third component selected from the group consisting of iron, zinc, zirconium and mixtures thereof.

U.S. Patent No. 5,001,267 to Speranza et al., teaches a process for forming secondary alkyl amine derivatives in a one-step reaction where ethylene-diamine is continuously mixed with a methyl alkyl ketone to form a reaction mixture which is continuously hydrogenated in the presence of a hydrogenation catalyst and hydrogen.

United Kingdom Patent No. 1,396,985 which issued June 11, 1975 teaches a process for the production of aliphatic or cycloaliphatic secondary or tertiary amines in which an aliphatic or cycloaliphatic carbonyl compound is reacted with an ammonia or an amine such as methylamine, cyclohexylamine, piperedine, morpholine, etc. in the presence of hydrogen and in the presence of a hydrogenation catalyst comprising a mixture of silver and palladium on a carrier which has been sintered by heating.

European Patent Application No. 409,116, filed July 14, 1990, teaches a process for the preparation of

acylic ethyleneamines which comprises reacting at least one of ammonia and ethylenediamine with monoethanolamine in the presence of a catalyst containing phosphoric acid or its condensate. Improved catalyst performance and the life of the catalyst can be prolonged in this process by feeding a phosphorus-containing material to the reaction system during the reaction.

In copending Champion et al., U.S. Patent Application Ser. No. 07/786,613, filed November 1, 1991, a process for preparing hydroxyalkyl N,N'-dialkylethylenediamines by reacting a N,N'-dialkylethylenediamine with an epoxide, such as ethylene oxide or propylene oxide in the presence of a catalytic amount of water at a temperature of about 25° to about 200° C and at a pressure of about 1 to about 70 atmospheres is described.

SUMMARY OF THE INVENTION

This invention relates to N-alkylethylene-diamines and to a continuous process for their preparation in which ethylenediamine is reacted with a long chain aliphatic aldehyde in the presence of hydrogen and a hydrogenation catalyst. Although other amine products as well are formed in the process, the desired N-alkylethylenediamine product is obtained in good yield and with high selectivity.

The compounds of this invention have the formula:

$$R\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2 \quad ,$$

where R is straight chain or branched alkyl of at least 7 carbon atoms and, preferably, ranges from 7 to about 17 carbon atoms.

The process for preparing the N-alkylethylene-diamines of this invention comprises reacting a long chain aliphatic aldehyde having at least 8 carbon atoms in a continuous manner with ethylene diamine in the presence of hydrogen and a hydrogenation catalyst at a temperature of about 100° to about 200° C and at a

pressure ranging from about 500 to about 4000 psig or more.

In conducting the reaction of this invention it is important that the correct proportion of the ethylenediamine and aldehyde reactants be employed. Preferably, the molar ratio of the aldehyde to the ethylenediamine will be in the range of about 1:1 to about 1:4 and more preferably in the range of about 1:1 to about 1:2.

The liquid hourly space velocity (LHSV) employed can be varied over a wide range and generally will range from about 0.5 to about 3.0 g/hr/cc-catalyst.

The reaction proceeds as shown below where, for purposes of illustration, the aldehyde employed is 2-ethylhexaldehyde:

$$C_4H_9CH(C_2H_5)CHO+H_2N-CH_2-CH_2-NH_2 \xrightarrow[\text{catalyst}]{H_2}$$

(A)

$$C_4H_9CH(C_2H_5)CH_2-NH-CH_2-CH_2-NH_2+H_2O$$

The major byproduct produced in reaction A is the corresponding alkyl amine, that is 2-ethylhexylamine,

along with small amounts of N,N'-di-2'-ethylhexyl-ethylenediamine and piperazine.

Useful long chain aldehydes which can be reacted in a continuous manner with ethylenediamine in the process of this invention include aliphatic aldehydes having at least 8 carbon atoms such as n-octyl aldehyde, 2-ethylhexyl aldehyde, n-decyl aldehyde, n-dodecyl aldehyde, octadecyl aldehyde, tetradecyl aldehyde, etc.

The N-alkylethylenediamine products of this invention are suitable for preparing a variety of chemical products such as polyurethanes, N-alkyl ethyleneureas, as intermediates in the preparation of detergents and in preparing imidazoles, such as 1-2'-ethylhexyl-2-methylimidazole, which are useful as catalysts for making polyurethanes, as catalysts for epoxide reactions, and as detergents and detergent intermediates.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

This process for the preparation of an N-alkylethylenediamine comprises continuously passing ethylenediamine, a long chain aldehyde having at least 8 carbon atoms and hydrogen over a hydrogenation catalyst at an elevated temperature and pressure. For example, ethylenediamine and the aldehyde can be pumped separately and combined into a single liquid feed stream before being introduced into the bottom of a suitable heated reactor, such as a tubular reactor containing a hydrogenation catalyst while hydrogen is simultaneously introduced into the reactor.

In this invention the reaction between the ethylenediamine and the aldehyde in the presence of hydrogen and a hydrogenation catalyst to form the desired N-alkylethylenediamine in good yield and selectively should be conducted continuously. Batch reactions favor the formation of other alkylamine products and the yield of the desired N-alkylethylenediamine is low. The products are recovered by distillation at reduced pressure. The pressure range most frequently employed is 5 to 50 mm. pressure.

Any suitable hydrogenation catalyst, preferably in pelleted form, may be used such as a catalyst comprising one or more of the metals of group VIIIB of the Periodic Table, such as cobalt, nickel, ruthenium, rhodium, palladium, platinum, mixed with one or more metals of group VIB of the Periodic Table such as chromium, molybdenum or tungsten. A promoter from group IB of the Periodic Table, such as copper, may also be included. As an example, a catalyst may be used comprising from about 60 to 85 mole percent of nickel, about 14 to 37 mole percent of copper and about 1 to about 5 mole percent of chromium, all calculated on an oxide free basis such as a catalyst disclosed in Moss U.S. Patent No. 3,151,112 or Yeaky U.S. Patent No. 3,654,370. As another example, a catalyst of the type disclosed in Boettger et al., U.S. Patent No. 4,014,933 may be used containing from about 70 to about 95 wt. % of a mixture of cobalt and nickel and from about 5 to about 30 wt. % of iron. As another example, a catalyst of the type disclosed in Habermann, U.S. Patent No. 4,152,353 may be used, such as a catalyst comprising nickel, copper and a third component which may be iron, zinc, zirconium or a mixture thereof, e.g., a catalyst containing from about 20 to about 45 wt. %

of nickel, about 36 to about 79 wt. % of copper, and about 1 to about 15 wt. % of iron, zinc, zirconium or a mixture thereof.

The following examples which illustrate various embodiments of the invention are not intended to be limitative.

EXAMPLE 1

(6770-77-2)

To a 300 cc Dowtherm® heated stainless steel tubular upflow reactor was charged 300 cc of pelleted nickel, copper, chromium catalyst as described in U.S. Patent No. 3,151,112. Ethylenediamine and 2-ethylhexaldehyde were pumped separately at LHSV of 1.06 g/hr-cc catalyst each and combined into a single liquid feed just before entering the bottom of the reactor. Hydrogen was charged to the bottom of the reactor at 100 % excess (based on the amount of aldehyde charged). The Dowtherm® temperature was maintained at 160° C. Reactor effluent was cooled and passed through a back-pressure regulator set to maintain 2500 psig pressure on the reactor. Effluent was then discharged into a receiver in which liquid product was collected at atmospheric pressure and from which gases were vented. The product was analyzed at ethylene-diamine and water free basis to contain 63.8 % of N-2'-ethylhexylethylenediamine (b.p. 64° C/10.2 mm/H_g), 2.3 % of N,N'-di-2-ethylhexylethylenediamine (b.p. 132° C/0.4 mm/H_g), 21.9 % of 2-ethylhexylamine, and 2.0 % of piperazine.

The reactor effluent may be distilled to isolate N-2'-ethylhexylethylenediamine or the water layer removed prior to distillation. A convenient method consists of adding cyclohexane and water to the reactor effluent. The organic layer (top layer) was separated from the aqueous layer and the organic layer washed with water to remove piperazine and ethylenediamine. The resulting organic layer was distilled to give the product.

EXAMPLE 2

(6770-77-3)

The procedure of Example 2 was followed except that the temperature was at 140° C. The product was analyzed at ethylenediamine and water free basis to contain 62.0 % of N-2'-ethylhexylethylenediamine, 3.0 % of N,N'-ethylhexylethylenediamine, 9.4 % of 2-ethylhexylamine, and 0.2 % of piperazine.

EXAMPLE 3

(6770-77B)

The procedure of Example 2 was followed except that the temperature was at 150° C. The product was analyzed at ethylenediamine and water free basis to

contain 66.1 % of N-2'-ethylhexylethylenediamine, 2.3 % of N,N'-2'-ethylhexylethylenediamine, 16.4 % of 2-ethylhexylamine and 0.2 % of piperazine.

EXAMPLE 4 (COMPARATIVE)

(6777-25 and 6777-34)

To a two-liter three-necked flask equipped with a stirrer, thermometer, additional funnel and Dean-Stark trap was charged 300 ml of cyclohexane and 240 g of ethylenediamine. About 520 g of 2-ethylhexaldehyde was added slowly at the temperature below 50° C. The mixture was heated to remove water through the Dean-Stark trap. The resulting reaction mixture (600 ml) along with 40 g of the nickel, copper, chromium catalyst of Example 1 was charged into a one-liter autoclave. After purging of air, to the autoclave was added hydrogen to a pressure of 1500 psig, heated to 180° C, and held at 180° C and 2500 psig until no further hydrogen pressure drop was noted. The product was analyzed at solvent and ethylenediamine free basis to contain 28.7 % of N-2'-ethylhexylethylenediamine, 8.3 % of N,N'-di-2-ethylhexylethylenediamine, 41.7 % of 2-ethylhexylamine and 3.4 % piperazine.

Comparative Example 4 shows that a substantially lower yield of the desired N-2'-ethylhexylethylene-diamine is obtained in the batch reaction as compared to the yield achieved in the continuous process of Examples 1 - 3.

EXAMPLE 5

(Usage Example)

To a 550 C Dowtherm® heated, stainless steel tubular downflow reactor was charged 200 cc of the nickel, copper, chromium catalyst used in Example 1. Then 300 cc of glass beads were placed on the top of the catalyst bed to serve as a preheat zone. A mixture with 1/1 mole ratio of acetic acid/N-2'-ethylhexyl-ethylenediamine was fed at LHSV of 0.57 g/hr-cc catalyst, atmospheric pressure, and 200° C (Dowtherm® temperature). The product was collected and distilled to give 75 % yield of 1-2'-ethylhexyl-2-methylimidazole (b.p. 108° C/018 mm H_g).

This imidazole product is useful as a curing agent for epoxy resins as more fully described in U.S. Patent Application, Ser. No. 07/877,915 of Waddill et al., filed May 4, 1992, which is incorporated herein by reference in its entirety.

nickel-copper-chromium catalyst comprises about 60 to about 85 mole % nickel, about 14 to about 37 mole % copper and about 1 to about 5 mole % chromium.

7. A process for preparing N-2-ethylhexyl-ethylenediamine which comprises continuously reacting 2-ethylhexaldehyde in the presence of hydrogen and a catalyst comprising about 60 to about 85 mole % nickel, about 14 to about 37 mole % copper and about 1 to about 5 % chromium, at a temperature of about 100° to about 200° C and a pressure of about 500 to about 4000 psig.

8. A compound of the formula:

$$R\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2 \quad ,$$

where R is alkyl of at least 7 carbon atoms.

9. The compound of Claim 8 wherein R is alkyl of from 7 to 17 carbon atoms.

10. The compound of Claim 8 wherein R is $-\underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{CH}}-C_4H_9$.